

U.S. PATENT APPLICATION

for

**LAYERED CATHODE MATERIALS FOR LITHIUM ION
RECHARGEABLE BATTERIES**

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LAYERED CATHODE MATERIALS FOR LITHIUM ION RECHARGEABLE
BATTERIES

CROSS-REFERENCE TO RELATED PATENT APPLICATIONS

[0001] This application claims the benefit under 35 U.S.C. 119(e) U.S. Provisional Patent Application No. 60/423,347, filed November 1, 2002, incorporated herein by reference in its entirety.

[0002] This invention was made with government support under Contract No. W-31-109-ENG-38 awarded to the Department of Energy. The Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

[0003] $\text{Li}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_2$ is a promising cathode material for Li-ion rechargeable batteries due to its lower cost, improved thermal safety performance, and lower toxicity compared with LiNiO_2 and LiCoO_2 . However, $\text{Li}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_2$ exhibits rather small capacity for high-energy applications and rather high impedance for high-power applications.

[0004] A need therefore remains for an improved layered cathode material for use with lithium ion rechargeable batteries.

SUMMARY OF THE INVENTION

[0005] It is therefore an object of the present invention to provide an improved cathode for rechargeable batteries that possesses improved impedance characteristics.

[0006] It is another object of the present invention to provide an improved cathode for rechargeable batteries that possesses improved stability of the layered oxide structure during electrochemical cycling.

[0007] It is still another object of the present invention to provide an improved cathode for rechargeable batteries that possesses improved capacity characteristics.

[0008] In accordance with the above objects, a number of materials with composition $\text{Li}_{1+x}\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma\text{M}'_\delta\text{O}_{2-z}\text{F}_z$ ($\text{M}' = \text{Mg, Zn, Al, Ga, B, Zr, Ti}$) have been developed for use with rechargeable batteries, wherein x is between about 0 and 0.3, α is between about 0.2 and 0.6, β is between about 0.2 and 0.6, γ is between about 0 and 0.3, δ is between about 0 and 0.15, and z is between about 0 and 0.2. Surface-coated $\text{Li}_{1+x}\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma\text{M}'_\delta\text{O}_{2-z}\text{F}_z$ ($\text{M}' = \text{Mg, Zn, Al, Ga, B, Zr, Ti}$) has also been developed, wherein x is between about 0 and 0.3, α is between about 0.2 and 0.6, β is between about 0.2 and 0.6, γ is between about 0 and 0.3, δ is between about 0 and 0.15, and z is between about 0 and 0.2. Extensive testing has been conducted to investigate the effect of adding the above metal and fluorine dopants and the surface modification on capacity, impedance, and stability of the layered oxide structure during electrochemical cycling.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIGURES 1(a)-1(c) show the morphology of $(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)$ -carbonate prepared by a co-precipitation method using ammonium hydrogen carbonate using magnification factors of $\times 500$, $\times 2,000$, and $\times 12,000$, respectively.

[0010] FIGURES 2(a)-2(c) show the morphology of $\text{Li}_{1+x}\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma\text{O}_2$ prepared by calcinations of $(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)$ -carbonate and lithium carbonate at

1000 °C for 10h in air, using magnification factors of $\times 1,000$, $\times 2,000$, and $\times 12,000$, respectively;

[0011] FIGURE 3 and FIGURE 4 are plots showing the X-ray diffraction patterns of various $\text{Li}_{1+x}\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma\text{M}'_\delta\text{O}_{2-z}\text{F}_z$ compounds;

[0012] FIGURE 5 is a plot showing the first charge/discharge curves of $\text{Li}/\text{Li}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_{2-z}\text{F}_z$ cells;

[0013] FIGURE 6 is a plot showing the cycling performance of $\text{Li}/\text{Li}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_{2-z}\text{F}_z$ cells;

[0014] FIGURE 7 is a plot showing the area specific impedance of $\text{C}/\text{Li}(\text{Ni}_\alpha\text{Mn}_\beta)\text{O}_{2-z}\text{F}_z$ cells as a function of state of charge measured by 30s-current interruption;

[0015] FIGURE 8 is a plot showing the variation of the area specific impedance values at 50% state of charge of $\text{C}/\text{Li}(\text{Ni}_\alpha\text{Mn}_\beta)\text{O}_{2-z}\text{F}_z$ cells;

[0016] FIGURES 9 and 10 show the cycling performance of uncoated $\text{Li}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_2$, $\text{Li}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_2$ coated with 0.5wt% Al-isopropoxide, and $\text{Li}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_2$ coated with 1.0wt% Al-isopropoxide at room temperature and 55°C, respectively;

[0017] FIGURE 11 shows the variation of area specific impedance (ASI) with cycling of $\text{C}/\text{Li}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_2$ measured by a 30s current interruption method;

[0018] FIGURE 12 shows the a.c. impedance spectroscopy of $\text{C}/\text{Li}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_2$ cells as a function of cycle number measured with $\text{C}/\text{Li}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_2$ cells;

[0019] FIGURE 13 presents the variation of area specific impedance at 60% SOC with a 55°C-storage time measured with $\text{C}/\text{Li}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_2$ cells;

[0020] FIGURE 14 is a plot showing the first charge/discharge curves and variation of discharge capacity with cycle number of $\text{Li/Li}_{1+x}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_2$ cells;

[0021] FIGURE 15 is a plot showing the area specific impedance of $\text{C/Li}_{1+x}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_2$ cells as a function of state of charge measured by a 30s current interruption method;

[0022] FIGURE 16 is a plot showing the cycling performance of $\text{Li/Li}_{1+x}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_{2-z}\text{F}_z$ cells at room temperature and at 55 °C; and

[0023] FIGURE 17 is a plot showing the area specific impedance of $\text{Li/Li}_{1+x}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_{2-z}\text{F}_z$ cells measured by a 30s current interruption method.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0024] The present invention presents layered lithium nickel manganese oxide cathode materials for lithium secondary batteries such as: (1) cathode materials doped with fluorine on oxygen sites to reduce impedance and to improve cycling stability at high temperature as well as at room temperature; (2) cathode materials doped with various metal ions on transition metal site to stabilize layered structure, suppress cation mixing and, consequently, improve electrochemical properties; lithium, cobalt, magnesium, zinc, aluminum, gallium, boron, zirconium, and titanium ions were chosen for the latter purposes; and (3) cathode materials surface-coated to improve cycling/power performance and thermal safety, wherein the coating element of the coating material source is at least one element selected from the group consisting of Al, Bi, Ga, Ge, In, Mg, Pb, Si, Sn, Ti, Tl, Zn, Zr. Either a solid-state reaction method or an aqueous solution method or a sol-gel

method may be employed for the preparation of the compounds

$Li_{1+x}Ni_{\alpha}Mn_{\beta}Co_{\gamma}M'^{\delta}O_{2-z}F_z$ with the value $M' = Mg, Zn, Al, Ga, B, Zr, Ti$.

[0025] For the solid state reaction method, (Ni,Mn,Co)-hydroxides or (Ni,Mn,Co)-carbonates may be prepared by a co-precipitation method. For preparation of (Ni,Mn,Co)-hydroxides, appropriate amount of $NiSO_4$ [or $Ni(CH_3COO)_{2-x}H_2O$ or $Ni(NO_3)_{2-x}H_2O$], $MnSO_4$ [or $Mn(CH_3COO)_{2-x}H_2O$ or $Mn(NO_3)_{2-x}H_2O$], and $CoSO_4$ [or $Co(CH_3COO)_{2-x}H_2O$ or $Co(NO_3)_{2-x}H_2O$] are dissolved in distilled water, and the solution is added to another solution of ammonium hydroxide (NH_4OH) and sodium hydroxide ($NaOH$) with a $pH = 10 \sim 12$. During the co-precipitation process, the pH of the overall solution is kept at $10 \sim 12$ using $NaOH$. For preparation of (Ni,Mn,Co)-carbonates, appropriate amount of $NiSO_4$ [or $Ni(CH_3COO)_{2-x}H_2O$ or $Ni(NO_3)_{2-x}H_2O$], $MnSO_4$ [or $Mn(CH_3COO)_{2-x}H_2O$ or $Mn(NO_3)_{2-x}H_2O$], and $CoSO_4$ [or $Co(CH_3COO)_{2-x}H_2O$ or $Co(NO_3)_{2-x}H_2O$] are dissolved in distilled water, and the solution is added to another aqueous solution of ammonium hydrogen carbonate [$(NH_4)_2HCO_3$]. During the co-precipitation process, the temperature of the overall solution is kept at $40 \sim 70^{\circ}C$. The co-precipitated powders are filtered and dried. To prepare a $Li_{1+x}Ni_{\alpha}Mn_{\beta}Co_{\gamma}M'^{\delta}O_{2-z}F_z$ ($M' = Mg, Zn, Al, Ga, B, Zr, Ti$) compound, appropriate amounts of lithium hydroxide (or lithium carbonate), lithium fluoride, (Ni,Mn,Co)-hydroxide [or (Ni,Mn,Co)-carbonate], and M' -hydroxides (or M' -oxides) are mixed. The mixed powders are calcined at $450 \sim 550^{\circ}C$ for 12-30 hours in air and then at $900 \sim 1000^{\circ}C$ for 10-24 hours either in air or in an oxygen-containing atmosphere.

[0026] For the aqueous solution method, appropriate amounts of lithium hydroxide, lithium fluoride, nickel hydroxide, cobalt hydroxide, and M' -hydroxide (or M' -nitrate) are dissolved in distilled water whose pH is adjusted

with nitric acid. An aqueous solution of manganese acetate is added to the above solution. The mixed solution is refluxed in a round bottom flask attached with a condenser at 80°C for about 12-24 hours and evaporated in a rotary vacuum evaporator. Organic contents in the gel precursor are eliminated at 400°C for 2 hours. Finally, the resulting powder is calcined at 900-1000°C for about 10-24 hours either in air or in an oxygen-containing atmosphere.

[0027] For the sol-gel method, appropriate amounts of lithium acetate, lithium fluoride, nickel acetate, manganese acetate, cobalt acetate, and M'-acetate are dissolved in distilled water and added to a glycolic/tartaric acid solution that is used as a chelating agent. The solution pH is adjusted to around 7 using ammonium hydroxide. The entire process is conducted under continuous stirring and heating on a hot plate. The resulting gel precursor is decomposed at 450°C for 5 hours in air. The decomposed powders are then fired at about 900-1000°C for about 10-24 hours either in air or in an oxygen-containing atmosphere.

[0028] For the surface-coating of the synthesized compound $\text{Li}_{1+x}\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma\text{M}'_\delta\text{O}_{2-z}\text{F}_z$, coating solutions are prepared by dissolving coating material sources in organic solvents or water. The coating material sources include A'-alkoxide, A'-salt or A'-oxide, where A' includes Al, Bi, Ga, Ge, In, Mg, Pb, Si, Sn, Ti, Tl, Zn, Zr or mixtures thereof. The coating solutions are mixed with the synthesized compound $\text{Li}_{1+x}\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma\text{M}'_\delta\text{O}_{2-z}\text{F}_z$ by an impregnation method such as dip coating. The amount of coating material sources may be between about 0.05 and 10 weight percent of $\text{Li}_{1+x}\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma\text{M}'_\delta\text{O}_{2-z}\text{F}_z$. Thereafter, the surface-coated $\text{Li}_{1+x}\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma\text{M}'_\delta\text{O}_{2-z}\text{F}_z$ powder is dried at temperatures between about 25°C and 700°C for approximately 1 to 24 hours.

[0029] The synthesized compound is mixed with a carbon additive and a PVDF binder to form a laminate film on an aluminum foil. This laminate is used for electrochemical testing in the presence of lithium or carbon counter electrodes and non-aqueous electrolytes made of LiPF₆/ EC:DEC (1:1).

[0030] FIGS. 1(a)-1(c) show the morphology of (Ni_αMn_βCo_γ)-carbonate prepared by the co-precipitation method using ammonium hydrogen carbonate. Spherical shape precursors with homogeneous size distribution are obtained by the co-precipitation. The magnification factors of FIGS. 1(a), 1(b), and 1(c) are ×500, ×2,000, and ×12,000, respectively.

[0031] FIGS. 2(a)-2(c) show the morphology of Li_{1+x}Ni_αMn_βCo_γO₂ prepared by calcinations of (Ni_αMn_βCo_γ)-carbonate and lithium carbonate at 1000°C for 10h in air. The spherical shape of the precursor is preserved after calcinations. The magnification factors of FIGS. 2(a), 2(b) and 2(c) are ×1,000, ×2,000, and ×12,000, respectively.

[0032] FIGS. 3 and 4 represent X-ray diffraction patterns of Li_{1+x}Ni_αMn_βCo_γM'_δO_{2-z}F_z compounds. All of the compounds exhibit the ordered rock-salt structure with crystallographic structure of $\bar{R}\bar{3}m$. For the Li-excess composition such as Li(Li_{0.2}Ni_{0.2+0.5z}Co_{0.1}Mn_{0.5-0.5z})O_{2-z}F_z, extra peaks appear at 20~25°, as shown in FIG. 4, which are generally attributed to cation ordering in the transition metal layer.

[0033] FIG. 5 shows the first charge/discharge curves of Li/Li(Ni_αMn_βCo_γ)O_{2-z}F_z cells, and FIG. 6 shows cycling performance of Li/Li(Ni_αMn_βCo_γ)O_{2-z}F_z cells. FIGS. 5 and 6 clearly show that the discharge capacity increases by more than 10%, and the cycling performance improves by the simultaneous substitution of cations and anions.

[0034] FIG. 7 shows area specific impedance (ASI) of $C/Li(Ni_{\alpha}Mn_{\beta})O_{2-z}F_z$ cells as a function of state of charge (SOC) measured by 30s-current interruption. FIG. 8 shows the variation of the ASI values at 50% SOC of $C/Li(Ni_{\alpha}Mn_{\beta})O_{2-z}F_z$ cells. FIGS. 7 and 8 clearly show that fluorine doping lowers impedance and enhances cycling stability.

[0035] FIGS. 9 and 10 show the cycling performance of uncoated $Li(Ni_{\alpha}Mn_{\beta}Co_{\gamma})O_2$, $Li(Ni_{\alpha}Mn_{\beta}Co_{\gamma})O_2$ coated with 0.5wt% Al-isopropoxide, and $Li(Ni_{\alpha}Mn_{\beta}Co_{\gamma})O_2$ coated with 1.0wt% Al-isopropoxide at room temperature and 55°C, respectively. The coating solution is prepared by dissolving appropriate amount of Al-isopropoxide in ethanol. $Li(Ni_{\alpha}Mn_{\beta}Co_{\gamma})O_2$ powders are then mixed thoroughly with the coating solution and dried at 100°C for 12h. The coated powders are subsequently heat-treated at 300°C for 3h in air. For FIG. 9, the data identified under group (a), $\alpha=0.4$, $\beta=0.4$, $\gamma=0.2$, with the $Li(Ni_{\alpha}Mn_{\beta}Co_{\gamma})O_2$ uncoated. For the data identified under group (b), $\alpha=0.4$, $\beta=0.4$, $\gamma=0.2$, and the $Li(Ni_{\alpha}Mn_{\beta}Co_{\gamma})O_2$ is coated with 0.5wt% Al-isopropoxide. For the data identified under group (c), $\alpha=0.4$, $\beta=0.4$, $\gamma=0.2$, and the $Li(Ni_{\alpha}Mn_{\beta}Co_{\gamma})O_2$ is coated with 1.0wt% Al-isopropoxide. In FIG. 10, for the data identified under group (a), $\alpha=0.4$, $\beta=0.4$, $\gamma=0.2$, with the $Li(Ni_{\alpha}Mn_{\beta}Co_{\gamma})O_2$ uncoated. For the data identified under group (b), $\alpha=0.4$, $\beta=0.4$, $\gamma=0.2$, and the $Li(Ni_{\alpha}Mn_{\beta}Co_{\gamma})O_2$ is coated with 0.5wt% Al-isopropoxide.

[0036] FIG. 11 shows the variation of area specific impedance (ASI) with cycling of $C/Li(Ni_{\alpha}Mn_{\beta}Co_{\gamma})O_2$ measured by a 30s current interruption method with $C/Li(Ni_{\alpha}Mn_{\beta}Co_{\gamma})O_2$ cells. The cells with coated cathode materials exhibit a very limited increase of ASI, whereas the cells with uncoated cathode material show a large impedance increase with cycling.

[0037] FIG. 12 shows the a.c. impedance spectroscopy of C/Li(Ni _{α} Mn _{β} Co _{γ})O₂ cells as a function of cycle number measured with C/Li(Ni _{α} Mn _{β} Co _{γ})O₂ cells. This representation indicates the surface coating significantly improves the stability of the cathode surface/electrolyte interface. In FIGS. 11 and 12, for the data identified under chart (a), $\alpha=0.4$, $\beta=0.4$, $\gamma=0.2$, with the Li(Ni _{α} Mn _{β} Co _{γ})O₂ uncoated. For the data identified under chart (b), $\alpha=0.4$, $\beta=0.4$, $\gamma=0.2$, and the Li(Ni _{α} Mn _{β} Co _{γ})O₂ is coated with 0.5wt% Al-isopropoxide. For the data identified under chart (c), $\alpha=0.4$, $\beta=0.4$, $\gamma=0.2$, and the Li(Ni _{α} Mn _{β} Co _{γ})O₂ is coated with 1.0wt% Al-isopropoxide.

[0038] FIG. 13 presents the impedance variation with a 55°C-storage time measured with C/Li(Ni _{α} Mn _{β} Co _{γ})O₂ cells. For the data identified under group (a), $\alpha=0.4$, $\beta=0.4$, $\gamma=0.2$, with the Li(Ni _{α} Mn _{β} Co _{γ})O₂ uncoated. For the data identified under group (b), $\alpha=0.4$, $\beta=0.4$, $\gamma=0.2$, and the Li(Ni _{α} Mn _{β} Co _{γ})O₂ is coated with 0.5wt% Al-isopropoxide. For the data identified under group (c), $\alpha=0.4$, $\beta=0.4$, $\gamma=0.2$, and the Li(Ni _{α} Mn _{β} Co _{γ})O₂ is coated with 1.0wt% Al-isopropoxide. FIGS. 9-13 clearly show the surface coating greatly improving the cycle life, as well as calendar life, of the lithium-ion cells.

[0039] FIG. 14 shows the first charge/discharge curves and variation of discharge capacity with cycle number of Li/Li_{1+x}(Ni _{α} Mn _{β} Co _{γ})O₂ cells. FIG. 15 shows the area specific impedance of C/Li_{1+x}(Ni _{α} Mn _{β} Co _{γ})O₂ cells as a function of state of charge measured by a 30s current interruption method.

[0040] FIG. 16 shows cycling performance of Li/Li_{1+x}(Ni _{α} Mn _{β} Co _{γ})O_{2-z}F _{z} cells at room temperature and at 55°C. FIG. 17 shows the area specific impedance of Li/Li_{1+x}(Ni _{α} Mn _{β} Co _{γ})O_{2-z}F _{z} cells measured by a 30s current interruption method.

[0041] FIGS. 14-17 clearly show that substitution of oxygen with fluorine significantly improves cycling performance and lowers the impedance of the cathode materials.

[0042] The materials described herein can be used as cathodes in lithium-ion rechargeable batteries for products such as electric vehicles, hybrid electric vehicles, portable electronics, and a variety of other products. The materials described herein are less expensive and thermally safer than existing cathode materials such as LiCoO_2 and LiNiO_2 . The materials of the present invention also exhibit improved calendar/cycle life when compared to existing cathode materials.

[0043] It should be understood that the above description of the invention and specific examples and embodiments, while indicating the preferred embodiments of the present invention are given by demonstration and not limitation. Many changes and modifications within the scope of the present invention may therefore be made without departing from the spirit thereof and the present invention includes all such changes and modifications.